

SPECIFICATION

Docket No. 20470.076

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN that we, Bradford G. Corbett, Sr., a citizen of the United States, residing in Fort Worth, Texas, and Jorge Arias, a citizen of Costa Rica, residing in San Jose, Costa Rica, have invented new and useful improvements in

PROTECTIVE COATING COMPOSITIONS AND TECHNIQUES FOR FLUID PIPING SYSTEMS

of which the following is a specification:

| | |
|--|-------------------------|
| <i>"EXPRESS MAIL" NO. EV 125792881 US</i> | |
| I hereby certify that this paper or fee is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10 on the date indicated below and is addressed to the Mail Stop: Patent Application, Comm. for Patents, P.O. Box 1450, Alexandria, VA 22313-1450. | |
| Date of Deposit: <u>Feb. 27, 2004</u> | By: <u>Sarah Horner</u> |

BACKGROUND OF THE INVENTION

1 **1. Cross Reference To Related Applications:** The present application claims priority from
2 provisional application serial number 60/506,074, filed September 24, 2003, entitled "Corrosion
3 Resistant Coating for Ductile Iron Pipe", by the same inventor.

4
5 **2. Field of the Invention:**

6
7 This invention relates generally to piping systems of the type used in fluid conveyance and, more
8 specifically, to coating compositions and techniques to protect such piping systems from deterioration
9 in the environment in which the pipes are stored and used.

10
11 **3. Description of the Prior Art:**

12
13 In one field of use, the present invention deals with corrosion protection of ferrous metal piping of
14 the type used in water, sewage, and other municipal fluid conveyance systems. By "ferrous metal" is
15 meant iron and alloys of iron. For example, one type of ferrous metal which is commonly encountered
16 in the waterworks industry is "ductile iron". This particular type of metal is widely used because it
17 offers a combination of a wide range of high strength, wear resistance, fatigue resistance, toughness
18 and ductility in addition to the well-known advantages of cast iron - castability, machinability,
19 damping properties, and economy of production. It takes its name from the fact that it is "ductile"
20 in nature, rather than being brittle, as was the case with earlier cast iron products and materials.
21 Other forms of "ferrous metals" include the following:

22
23 White Iron-

24 White iron is fully carbidic in its final form. The presence of different carbides, produced by alloying,
25 makes white iron extremely hard and abrasion resistant but very brittle.

Gray Iron-

Gray iron is by far the oldest and most common form of cast iron. As a result, it is assumed by many to be the only form of cast iron and the terms "cast iron" and "gray iron" are used interchangeably. Gray iron, named because its fracture has a gray appearance, consists of carbon in the form of flake graphite in a matrix consisting of ferrite, pearlite or a mixture of the two. The fluidity of liquid gray iron, and its expansion during solidification due to the formation of graphite, have made this metal ideal for the economical production of shrinkage-free, intricate castings. The presence of graphite flakes in the microstructure also gives gray iron excellent machinability, damping characteristics and self-lubricating properties.

Malleable Iron-

Unlike gray and ductile iron, malleable iron is cast as a carbide or white iron and an annealing or "malleablizing" heat treatment is required to convert the carbide into graphite. The microstructure of malleable iron consists of irregularly shaped nodules of graphite in a matrix of ferrite and/or pearlite. The presence of graphite in a sphere-like form gives malleable iron ductility and strength almost equal to cast, low-carbon steel.

Despite the early availability of the various forms of iron discussed above, developers continued to strive for a cast "gray iron" with mechanical properties equal or superior to malleable iron. The solution to this quest was initially found in the addition of magnesium (as a copper-magnesium alloy) to cast iron. The resulting solidified castings contained not flakes, but nearly perfect spheres of graphite, and marked the inception of ductile iron. In experimental work which followed, the production of spherical graphite in hypereutectic gray iron was also achieved by the addition of small amounts of cerium. Today, grades of ductile iron are available offering the option of choosing high ductility, with grades guaranteeing more than 18% elongation, or high strength, with tensile strengths exceeding 120 ksi (825 MPa). austempered ductile iron (ADI), offers even greater mechanical properties and wear resistance, providing tensile strengths exceeding 230 ksi (1600 MPa).

1 As a result of the above described advantages of ductile iron, it has become widely adopted in the
2 waterworks industry. One disadvantage of pipes, components, accessories and fittings (piping
3 systems) made from ductile iron, however, is that such products are subject to corrosion and
4 degradation in the normal storage and work environment. For example, lengths of pipe, as well as
5 glands, fittings and restraint mechanisms if the type commonly used in the waterworks industry are
6 typically stored prior to use at a warehouse or in a field location. Moisture and oxidation inevitably
7 cause rust and corrosion.

8
9 Corrosion affects not only the appearance of ferrous metals used in fluid conveyance systems, but
10 can also rust, pit, scar or otherwise degrade the exposed surfaces of such materials. As a result,
11 various coating technologies have been developed over the years to combat the problem of corrosion
12 in fluid conveyance systems. One commonly used coating material is comprised of asphalt or asphalt
13 derivatives. Asphalt-based coating compositions have been used for many years to coat ductile iron
14 or metallic or partially metallic pipes, conduits, tubing and the like. As a pipe coating, asphalt-based
15 coating compositions function to provide corrosion-resistance, sealing and for making pipes more
16 water-resistant. However, most asphalt-based pipe coating compositions which exhibit sufficient
17 coating properties are formed with solvent-based solutions of asphalt and mineral spirits. While these
18 coatings are minimally acceptable for their intended purposes, they release volatile organic
19 compounds (VOCs) while drying. The VOC release can be very significant such that, during the pipe
20 manufacturing process in which the coatings are applied, pipe production must either occasionally
21 be curtailed to avoid VOC releases in excess of EPA standards or EPA fines may be incurred.

22
23 Asphaltic aqueous emulsions which do not release VOCs are known, but to date have generally not
24 exhibited the necessary properties which facilitate their use as a coating composition for ferrous
25 piping and components. The thickness and shear sensitivity of aqueous asphalt emulsions, as well as
26 other mechanical properties, have generally prevented their use as a direct pipe surface coating in the
27 past. Problems have also been encountered in the past with the known emulsion type coatings with
28 respect to the ability of the emulsions to achieve good adhesion directly to the pipe surface. Certain

1 of the components of the emulsions have proven to be degradable in the presence of, oily substances
2 encountered on some pipe or other surfaces. The emulsions also tend to be temperature sensitive
3 which can create problems when trying to achieve manufacturing coating uniformity in year-round
4 pipe manufacture. Due to the shear sensitivity and poor adhesion properties, it is also difficult to
5 apply many of the prior art emulsions to a pipe surface, to avoid "sag" caused by gravity during the
6 setting process.

7
8 Another type coating technology which has been used in the past in the waterworks industry is the
9 use of cement-mortar linings. Today ductile iron pipes are routinely centrifugally lined at the factory
10 in an attempt to assure that a uniform thickness of cement-mortar is distributed throughout the entire
11 length of pipe in order to provide protection from corrosion. The principal standard covering cement
12 lining is ANSI/AWWA C104/A21.4. Cement-lined pipe is also furnished for some sewage service
13 and a number of other applications. There are also problems with cement-mortar lined pipes,
14 however. AWWA C104 allows for surface crazing and cracks of a specified nature and magnitude.
15 In many instances, unacceptable cracks and looseness in cement linings occur prior to installation,
16 particularly where pipe is stored for a considerable time.

17
18 In another field of use, the present invention deals with steel pipe, components and accessories of the
19 type which would be used, for example, in the oil and gas industries. A large variety of "oil field
20 tubular goods" such as drill pipe, casing, tubing, line pipe and couplings are known in the industry
21 which could be treated with the improved metal treatment of the invention. The protective coating
22 of the invention would provide protection for oil field tubular goods from deterioration at storage
23 locations as well as during use in such adverse environments as salt and hydrogen sulfide.

24
25 A need exists, therefore, for an improved technique for protecting ferrous metal piping systems of
26 the type used in fluid conveyance from corrosion and other detrimental environmental factors present
27 in the field or in the manufacturing or storage facility.

1 A need exists for such an improved technique which could be used to provide improved corrosion
2 protection for ductile iron pipe of the type used in fluid conveyance systems and particularly in the
3 waterworks industry.

4
5 A need exists for such a coating system which is simple and economical to apply and which provides
6 adequate corrosion resistance to water and sewer lines which are buried in underground locations in
7 normal use, or which are being held in a storage location at the manufacturing facility or at a field
8 location.

9
10 A need also exists for such a coating system which provides adequate corrosion resistance to the
11 glands, fittings, repair clamps and bands, and other associated components and accessories of such
12 piping systems used for fluid conveyance.

13
14 A need also exists for such a coating system which could be used to coat the metal surfaces of oil
15 field tubular goods of the type used in the oil and gas industries.

SUMMARY OF THE INVENTION

The present invention, among other things, provides an asphalt-free ferrous metal piping system which resists corrosion in the work or storage environment for an extended period of time.

The technique of the present invention provides effective corrosion protection for a variety of ferrous metal piping components without releasing VOCs such that environmental compliance is facilitated in the manufacture of coated surfaces such as in manufacturing coated pipes to provide physical protection and corrosion-resistance.

In one aspect, the present invention provides a component of a ferrous metal piping system, such as a waterworks pipe, with improved corrosion resistance. The pipe includes a pipe body formed of a ferrous metal, the pipe body having an exterior surface and an interior surface, a length and opposing end openings. A corrosion resistant coating is applied to at least a selected one of the exterior and interior surfaces, the corrosion resistant coating comprising an aqueous phenolic resin dispersion.

The preferred aqueous phenolic resin dispersion is a high molecular weight resin that is modified to include pendant ionic moieties on a phenolic backbone structure. The coating preferably comprises a continuous aqueous phase and, dispersed within the aqueous phase, the reaction product of a phenolic resin precursor and a modifying agent, wherein the modifying agent includes at least one ionic group and at least one functional moiety that enables the modifying agent to undergo condensation with the phenolic resin precursor. The resulting dispersed phenolic resin reaction product includes at least one phenolic ring to which is bound the ionic group from the modifying agent. The preferred modifying agents may include an aromatic compound or a sulfate, sulfonate, sulfinic, sulfenyl or oxysulfonate and the reactive functional moiety can be a hydroxy or hydroxyalkyl.

1 The ferrous metal piping system can also include an accessory or component of the ductile iron pipe.
2 For example, the accessory or component may include glands, fittings, mechanical joints, swivel
3 hydrant fittings, push-on fittings, service boxes, valves, valve boxes, meter boxes, restraint joint
4 devices, nuts, bolts and external wedge devices, and the like. In the case of an accessory component,
5 the component typically has a ferrous metal body having an exposed exterior surface. The corrosion
6 resistant coating is applied to at least the exposed exterior surface, the corrosion resistant coating
7 comprising an aqueous phenolic resin dispersion.

8
9 In the preferred treatment technique, at least an exposed metal surface of the ferrous metal device is
10 coated with a corrosion resistant coating by subjecting the exposed metal surface to a treatment
11 solution which comprises an aqueous phenolic resin dispersion as described above and optionally an
12 acid and a flexibilizer. Preferably, the ferrous metal device is dipped into a treatment solution which
13 includes the aqueous phenolic resin dispersion and at least an acid. One preferred acid is phosphoric
14 acid. The preferred phenolic resin can be selected from the group consisting of novolak resins and
15 resole resins. By dipping the ferrous metal device into a bath of the aqueous phenolic dispersion and
16 acid, the coating autodeposits onto the exposed metal surface.

17
18 The invention further includes a ferrous metal pipe, component or accessory of the type used in the
19 waterworks industry which consists essentially of the ferrous metal having a surface for coating and
20 a coating applied to the surface and formed from a coating composition which comprises Lord
21 METALJACKET™ Coating sold by Lord Corporation of 1625 Riverfork Drive East, Huntington,
22 IN 46750.

23
24 The invention also includes an improved method for protecting a ferrous metal pipe, component or
25 accessory of the type used in the waterworks industry by applying a coating composition to the
26 surface of the ferrous metal and allowing the coating composition to solidify, wherein the
27 improvement comprises providing as the coating composition a coating which comprises Lord

METALJACKET™ Coating sold by Lord Corporation of 1625 Riverfork Drive East, Huntington,
IN 46750.

In another aspect, the present invention provides a protective coating for oil field tubular goods such
as drill pipe, casing, tubing, line pipe and couplings.

Additional objects, features and advantages will be apparent in the written description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an end view of a gland in place on a section of ductile iron pipe which gland and pipe have been treated with a corrosion resistant coating according to the technique of the present invention.

Figure 2 is a partial cross sectional view of the pipe and gland of Figure 1 showing the bolts which are used to form a secure joint of pipe in the fluid conveyance system.

Figure 3 is a simplified flow diagram of the technique of the invention as used to coat a gland for a mechanical restraint system for a ferrous metal pipe used in a fluid conveyance system.

DETAILED DESCRIPTION OF THE INVENTION

The techniques of the present invention are used for coating metal piping systems of the type used in fluid conveyance, such as ductile iron pipes, components and accessories used in the waterworks industry. In another field of endeavor, the techniques of the invention can be applied to steel pipe and components such as drill pipe, casing and tubing used in the oil and gas industries. The coating techniques of the invention are particularly useful in coating the surface of a pipe to provide, for example, corrosion resistance to a surface, protecting the underlying surface from physical degradation, rust and corrosion, and rendering the surface water-resistant. The technique of the invention will first be described with reference to the waterworks industry and ductile iron pipe. However, the techniques can also be applied to components and accessories, including but not limited to glands, fittings, mechanical joints, repair clamps, swivel hydrant fittings, push-on fittings, service boxes, valve boxes, meter boxes, restraint joint devices, nuts, bolts, external wedge devices, as well as other accessories and components formed of ferrous metals and steel used in the water works industry.

The coating techniques of the invention are particularly adapted for protecting surfaces of ferrous metals, i.e., iron and iron alloys, and more particularly, for coating pipe such as ductile iron pipe. The coating techniques of the invention are useful for coating both the interior and the exterior of a pipe, component or accessory of a ferrous metal piping system. The surface may be arcuate, such as the exterior surface of a pipe, flat or an irregular geometry. While the coating is well suited for use on curved and arcuate pipe surfaces, due to its setting characteristics and lack of "sag", the coating is not specifically limited to use on any particular surface geometry.

The preferred ferrous metals to be treated with the treatment system of the invention are ductile irons. The modern ductile iron family includes materials offering a range of properties which can be generally described as follows:

1 **Ferritic Ductile Iron-**

2 This form of the metal is characterized by graphite spheroids in a matrix of ferrite which provide an
3 iron with good ductility and impact resistance and with a tensile and yield strength equivalent to a low
4 carbon steel. Ferritic ductile iron can be produced "as-cast" but may be given an annealing heat
5 treatment to assure maximum ductility and low temperature toughness.

6
7 **Ferritic Pearlitic Ductile Iron-**

8 These are the most common grades of ductile iron and are normally produced in the "as cast"
9 condition. The graphite spheroids are in a matrix containing both ferrite and pearlite. The properties
10 of this iron are intermediate between ferritic and pearlitic grades, with good machinability and low
11 production costs.

12
13 **Pearlitic Ductile Iron-**

14 This metal is characterized by graphite spheroids in a matrix of pearlite with the result being an iron
15 with high strength, good wear resistance, and moderate ductility and impact resistance.
16 Machinability is also superior to steels of comparable physical properties.

17
18 The preceding three types of ductile iron are the most common and are usually used in the as-cast
19 condition, but ductile iron can be also be alloyed and/or heat treated to provide the following grades
20 for a wide variety of additional applications:

21
22 **Martensitic Ductile Iron-**

23 This type of ductile iron is produced by using sufficient alloy additions to prevent pearlite formation,
24 and a quench-and-temper heat treatment. The resultant tempered martensite matrix develops very
25 high strength and wear resistance but with lower levels of ductility and toughness.

1 Bainitic Ductile Iron-

2 This grade can be obtained through alloying and/or by heat treatment to produce a hard, wear
3 resistant material.

4
5 Austenitic Ductile Iron-

6 Alloyed to produce an austenitic matrix, this ductile iron offers good corrosion and oxidation
7 resistance, good magnetic properties, and good strength and dimensional stability at elevated
8 temperatures.

9
10 Austempered Ductile Iron (ADI)-

11 ADI, is a more recent addition to the ductile iron family, and is a sub-group of ductile irons produced
12 by giving conventional ductile iron a special austempering heat treatment. Nearly twice as strong as
13 pearlitic ductile iron, ADI still retains high elongation and toughness. This combination provides a
14 material with superior wear resistance and fatigue strength.

15
16 As mentioned above, the techniques of the invention can also be applied to iron pipe, steel pipe and
17 components, such as the steel pipe commonly used in the oil and gas industries. Down hole tubulars
18 are typically formed of carbon alloy steel but may also be formed of more exotic materials such as
19 corrosion resistant alloy materials (CRA). The oil and gas industry is constantly seeking new ways
20 to efficiently and economically increase production of hydrocarbon fluids and decrease corrosion of
21 oil field tubular goods. There are various ways to approach this challenge, many of which involve
22 improvements to the oil country tubular goods, or down-hole tubulars, through which the fluids flow
23 to the surface. There are many different factors that affect the performance of down-hole tubulars
24 and reduce fluid flow rates including: pipe corrosion, clogging, and fluid flow friction. Corrosion
25 occurs when a corrosive agent attacks and deteriorates the inside diameter surface of the down-hole
26 tubular, resulting in a shortened operational life and high maintenance costs. Clogging is the
27 accumulation of sludge and debris, such as paraffin and scale, on the inside diameter surface.
28 Clogging results in restricted flow and reduced production. Fluid flow friction in down-hole tubulars

1 creates significant pressure losses, resulting in reduced flow rates and decreased fluid production.
2 If these three flow-rate reducing factors could be reduced or eliminated, fluid production could be
3 increased, maintenance time and costs could be reduced, operational life could be extended, and
4 smaller diameter production tubing could be used to produce the same amount of fluids that are
5 currently being produced through larger diameter production tubing.

6
7 Obviously, from a corrosion standpoint, the replacement of steel tubulars and associated hardware
8 with materials less subject to corrosion would be highly desirable in gas and oil field applications, if
9 it were practical. While the use of corrosion resistant alloys for corrosion control have demonstrated
10 superior corrosion resistance properties, they are quite costly and exhibit complex manufacturing and
11 handling constraints. Non-metallic components, such as fiberglass casing, tubing, sucker rods and
12 the like are finding their way into oil field applications. Performance limitations, including service
13 loads, pressures and temperatures, restrict the across-the-board replacement of metallic hardware,
14 however. The present invention provides improved corrosion protection for oilfield tubular goods,
15 including those formed of carbon alloy steel.

16
17 In describing the advantages of the compositions and techniques of the invention, it is perhaps best
18 to review the prior art attempts to protect piping systems of the type under consideration involving
19 the use of adhesive type coatings. Commercialization of adhesive compositions of this general type
20 began in the 1940s. These adhesive systems consisted of a primer and a cover coat. In applying the
21 adhesive system, it was first necessary to prepare the metal substrate for bonding. The traditional
22 methods for preparing steel substrates include either grit blasting or phosphatizing. In grit blasting,
23 the first step is to either vapor degrease or alkaline clean the steel part to remove the drawing oils and
24 organic contaminants. The next step involves blasting the surface with either steel shot or aluminum
25 oxide. This step removes the oxides that have formed on the surface. This is followed by a second
26 vapor or alkaline degreasing step to remove any oils or contaminants that could have been put on the
27 part during the blasting operation.

1 The second most commonly used method for preparing steel parts was the use of a zinc phosphate
2 coating to provide some enhanced corrosion resistance. Typically, either a microcrystalline or
3 calcium modified zinc phosphate was used to treat the steel parts. The process for applying a
4 phosphate coating involves removing the oily contaminants with an alkaline cleaner that is then
5 followed by several rinses. An acid pickle is then used to remove the oxides from the surface of the
6 steel. Again, several rinses are employed to remove the residual chemistry and provide a clean,
7 workable surface. The steel parts are then placed in the zinc phosphate bath. Once the zinc
8 phosphate is applied, the parts are rinsed and placed in a rust inhibiting sealer. This sealer fills in the
9 pores of the phosphate to further prevent rusting. The final step involves a hot air dry to remove the
10 remaining water. The parts are now ready for primer and cover coat adhesive application.

11
12 The techniques of the invention bear some similarity to the above described process steps of zinc
13 phosphating steel. However, the coating techniques of the invention utilize a unique class of coating
14 composition which eliminates many of the drawbacks associated with traditional zinc phosphating.
15 Specifically, the techniques of the invention eliminate much of the hazardous waste and sludge that
16 is generated during the traditional phosphating process as well as the elimination of objectionable
17 VOC's. Several trends that have occurred in the last decade have focused increased pressure to
18 reduce volatile organic and hazardous waste emissions in all phases of industry.

19
20 In a first aspect of the corrosion protection technique of the invention, a pipe, component or
21 accessory of a ferrous metal piping system is coated with a corrosion resistant coating which is
22 applied to at least a selected exposed surface thereof, the corrosion resistant coating comprising an
23 aqueous phenolic resin dispersion. The preferred aqueous phenolic resin dispersion is a high
24 molecular weight resin that is modified to include pendant ionic moieties on a phenolic backbone
25 structure. The coating preferably comprises a continuous aqueous phase and, dispersed within the
26 aqueous phase, the reaction product of a phenolic resin precursor and a modifying agent, wherein the
27 modifying agent includes at least one ionic group which aids in maintaining the stability of the
28 aqueous dispersion and at least one functional moiety that enables the modifying agent to undergo

1 condensation with the phenolic resin precursor. The resulting dispersed phenolic resin reaction
2 product includes at least one phenolic ring to which is bound the ionic group from the modifying
3 agent. Preferred modifying agents include aromatic compounds as well as a sulfate, sulfonate,
4 sulfinic, sulfenyl or oxysulfonate with the preferred reactive functional moiety being a hydroxy or
5 hydroxyalkyl.

6
7 One commercially available phenolic resin dispersion is sold commercially by Lord Corporation under
8 the METALJACKET™ family of coatings. Formulation of one suitable phenolic resin dispersion for
9 purposes of the present invention can be described with reference to the following issued U.S.
10 Patents: 6,130,289; 6,383,307; 6,476,119; and 6,521,687, the disclosure of which is incorporated
11 herein by reference to the extent that it is not reproduced in the written description which follows. The
12 formulation and use of this family of aqueous based, phenolic resin dispersions will be recapped below
13 with reference primarily to issued U.S. Patent No. 6,383,307, issued May 7, 2002, to Kucera et al.,
14 entitled "Aqueous Metal Treatment Composition" and U.S. Patent No. 6,130, 289, issued October
15 10, 2002, to Kucera, entitled "Aqueous Phenolic Dispersion."

16
17 Description of METALJACKET™ Chemistry:

18
19 The family of aqueous phenolic dispersions which are useful in practicing will first be described with
20 respect to the above mentioned METALJACKET™ family of coatings. These coatings are highly
21 reactive, highly functional, hydrophilic phenolic resins which can be stabilized in an aqueous phase
22 by modifying the phenolic resins to incorporate aromatic rings that have ionic pendant groups onto
23 the phenolic resin structure. For example, the first component of the formulation can be a novolak
24 resin. This resin is responsible for the autodeposition characteristic of the metal treatment
25 composition which will be described. The phenolic novolak resin dispersion can be obtained by
26 initially reacting or mixing a phenolic resin precursor and a modifying agent, theoretically producing
27 a condensation reaction between the phenolic resin precursor and the modifying agent. The phenolic
28 resin precursors can include both novolak and resole resins. However, the resole resins cannot be

1 used in or formulated into the metal treatment where the treatment also includes an acid component,
2 as will be described. Under the acidic conditions of the metal treatment resoles are unstable.

3
4 The aqueous dispersions also contain a "modifying agent" with two functional moieties. One
5 functional moiety of the modifying agent provides the ionic pendant group that enables stable
6 dispersion of the phenolic resin. Without the ionic pendant group, the phenolic resin would be unable
7 to maintain a stable dispersion in water.

8
9 The other important functional moiety in the modifying agent enables the modifying agent to react
10 with the phenolic resin precursor. The modifying agent can contain more than one ionic pendant
11 group and more than one reaction-enabling moiety.

12
13 Incorporation of aromatic sulfonate functional moieties into the phenolic resin structure via
14 condensation is one method of providing the ionic pendant groups. Accordingly, one class of ionic
15 moieties are substituents on an aromatic ring that include a sulfur atom covalently or ionically bonded
16 to a carbon atom of the aromatic ring. Another example of a covalently bound substituent is sulfate
17 ion. Sulfonate is one preferred ionic group.

18
19 The reaction-enabling functional moiety of the modifying agent can be any functional group that
20 provides a site on the modifying agent for undergoing condensation with a phenolic resin. If the
21 phenolic resin precursor is a resole, the modifying agent reacts with an alkylol or benzyl ether group
22 of the resole. If the modifying agent is aromatic, the reaction-enabling functional moiety is a
23 substituent on the aromatic ring that causes a site on the ring to be reactive to the alkylol or benzyl
24 ether of the resole precursor. An example of such a substituent is a hydroxy or hydroxyalkyl, with
25 hydroxy being preferred. The hydroxy- or hydroxyalkyl-substituted aromatic modifying agent is
26 reactive at a site ortho and/or para to each hydroxy or hydroxyalkyl substituent. In other words, the
27 aromatic modifying agent is bonded to, or incorporated into, the phenolic resin precursor at sites on
28 the aromatic ring of the modifying agent that are ortho and/or para to a hydroxy or hydroxyalkyl

1 substituent. At least two reaction-enabling functional moieties are preferred to enhance the reactivity
2 of the aromatic modifying agent with the phenolic resin precursor.

3
4 Alternatively, the reaction-enabling functional moiety of the modifying agent can be a formyl group,
5 preferably attached to a carbon atom of an aromatic ring. In this instance, the phenolic resin
6 precursor is a novolak rather than a resole. The novolak precursor is reacted via an acid catalyzed
7 aldehyde condensation reaction with the formyl group-containing modifying agent so that the formyl
8 group forms a divalent methylene linkage to an active site on an aromatic ring of the backbone
9 structure of the novolak precursor. Consequently, the modifying agent structure (including the ionic
10 moiety) is incorporated into the phenolic structure through the generated methylene linkage.

11
12 Another alternative reaction-enabling functional moiety could be a diazo group, preferably attached
13 to a carbon atom of an aromatic ring. In this instance, the phenolic resin precursor is a novolak rather
14 than a resole. The novolak precursor is reacted via a diazo coupling reaction with the diazo group-
15 containing modifying agent so that the diazo group forms a divalent diazo linkage to an active site
16 on an aromatic ring of the backbone structure of the novolak precursor. Consequently, the modifying
17 agent structure (including the ionic moiety) is incorporated into the phenolic structure through the
18 diazo linkage.

19
20 The modifying agent also can optionally include a functional moiety that is capable of chelating with
21 a metal ion that is present on a substrate surface on which the phenolic resin dispersion is applied.
22 The chelating group remains as a residual group after the condensation of the phenolic resin precursor
23 and the aromatic modifying agent. Typically, the chelating group is a substituent on the aromatic ring
24 that is capable of forming a 5- or 6-membered chelation structure with a metal ion. Examples of such
25 substituents include hydroxy and hydroxyalkyl, with hydroxy being preferred. At least two such
26 functional groups must be present on the modifying agent molecule to provide the chelating. In the
27 case of an aromatic modifying agent, the chelating groups should be located in an ortho position
28 relative to each other.

1
2 An aromatic modifying agent is particularly advantageous. Preferably, the ionic group and the
3 reaction-enabling moiety are not substituents on the same aromatic ring. The ionic group, particularly
4 sulfonate, appears to have a strong deactivating effect on condensation reactions of the ring to which
5 it is attached. Consequently, an ionic group attached to the same ring as the reaction-enabling moiety
6 would not allow the modifying agent to readily react with the phenolic resin. However, it should be
7 recognized that this consideration for the location of the ionic and reaction-enabling moieties is not
8 applicable to the formyl group-containing modifying agent and diazo modifying agent.

9
10 Illustrative aromatic modifying agents include salts of 6,7-dihydroxy-2-naphthalenesulfonate; 6,7-
11 dihydroxy-1-naphthalenesulfonate; 6,7-dihydroxy-4-naphthalenesulfonate; Acid Red 88; Acid Alizarin
12 Violet N; Erichrome Black T; Erichrome Blue Black B; Brilliant Yellow; Crocein Orange G; Biebrich
13 Yellow; and Palatine Chrome Black 6BN. 6,7-dihydroxy-2-naphthalenesulfonate, sodium salt is the
14 preferred aromatic modifying agent.

15
16 Any phenolic resin could be employed as the phenolic resin precursor, but it has been found that
17 resoles are especially suitable. The resole precursor should have a sufficient amount of active alkylol
18 or benzyl ether groups that can initially condense with the modifying agent and then undergo further
19 subsequent condensation. The phenolic resin precursor has a lower molecular weight than the final
20 dispersed resin since a the precursor undergoes condensation to make the final dispersed resin.
21 Resoles are prepared by reacting a phenolic compound with an excess of an aldehyde in the presence
22 of a base catalyst.

23
24 The reactants, conditions and catalysts for preparing resoles suitable for the resole precursor of the
25 present invention are well-known. The phenolic compound can be any of those previously listed or
26 other similar compounds, although multi-hydroxy phenolic compounds are undesirable. Particularly
27 preferred phenolic compounds for making the resole precursor include phenol per se and alkylated
28 phenol. The aldehyde also can be any of those previously listed or other similar compounds, with

1 formaldehyde being preferred. Low molecular weight, water soluble or partially water soluble resoles
2 are preferred as the precursor because such resoles maximize the ability to condense with the
3 modifying agent. The F/P ratio of the resole precursor should be at least 0.90. Illustrative
4 commercially available resoles that are suitable for use as a precursor include a partially water soluble
5 resole available from Georgia Pacific under the trade designation BRL 2741 and a partially water
6 soluble resoles available from Schenectady International under the trade designations HRJ11722 and
7 SG3100.

8
9 Preferably, the dispersed novolak is produced by reacting or mixing 1 mol of modifying agent(s) with
10 2-20 mol of phenolic resin (preferably resole) precursor(s) and, preferably, 2-20 mol of multi-hydroxy
11 phenolic compound(s). An aldehyde compound, preferably formaldehyde, is also required to make
12 the novolak. The aldehyde compound can optionally be added as a separate ingredient in the initial
13 reaction mixture or the aldehyde compound can be generated in situ from the resole precursor. The
14 resole precursor(s), multi-hydroxy phenolic compound(s) and modifying agent(s) co-condense to
15 form the dispersed novolak. The reaction typically is acid catalyzed with an acid such as phosphoric
16 acid. The F/P ratio of aldehyde compound(s) to combined amount of resole precursor(s) and multi-
17 hydroxy phenolic compound(s) in the initial reaction mixture preferably is less than 0.9. Preferably,
18 synthesis of the dispersed novolak is a two stage reaction. In the first stage, the resole precursor(s)
19 is reacted with the modifying agent(s) and, optionally, a small amount of multi-hydroxy phenolic
20 compound(s). Once this first stage reaction has reached the desired point (i.e. the resin can be readily
21 formed into a translucent dispersion), the acid catalyst and a greater amount of multi-hydroxy
22 phenolic compound(s) is added to the reaction mixture. Pyrocatechol (also simply known as
23 catechol) is a preferred multi-hydroxy phenolic compound for reacting in the first stage and resorcinol
24 is a preferred multi-hydroxy phenolic compound for reacting in the second stage.

25
26 Hydrophilic novolaks typically have a hydroxy equivalents of between 1 and 3 per aromatic ring.
27 Preferably, dispersed hydrophilic novolaks useful for the present purposes have a hydroxy equivalents
28 of 1.1 to 2.5, more preferably 1.1 to 2.0. The hydroxy equivalents is calculated based on the amount

1 of multi-hydroxy phenolic compounds used to make the novolak.

2
3 If the modifying agent includes a sulfur-containing ionic group, the resulting modified phenolic resin
4 should have a carbon/sulfur atom ratio of 20:1 to 200:1, preferably 20:1 to 100:1. If the sulfur
5 content is greater than the 20:1 carbon/sulfur atom ratio, the modified phenolic resin begins to become
6 water soluble, is more stable with respect to multivalent ions and is difficult to thermoset. These
7 characteristics are adverse to the preferred use of the phenolic resin dispersion. If the sulfur content
8 is below the 200:1 carbon/sulfur atom ratio, then the resin dispersion cannot maintain its stability.
9 Viewed another way, the dispersed phenolic resins have 0.01 to 0.10, preferably 0.03 to 0.06,
10 equivalents of sulfonate functionality/100 g resin. The aqueous dispersion of the phenolic resin
11 preferably has a solids content of 1 to 50, preferably 15 to 30.

12
13 The modifying agent and the phenolic resin precursor can be reacted under conditions effective to
14 promote condensation of the modifying agent with the phenolic resin precursor. The reaction is
15 carried out in water under standard phenolic resin condensation techniques and conditions. The
16 reactant mixture (including water) generally is heated from 50 to 100 degree C. under ambient
17 pressure, although the specific temperature may differ considerably depending upon the specific
18 reactants and the desired reaction product. The resulting product is a concentrate that is self-
19 dispersible upon the addition of water and agitation to reach a desired solids content. The final
20 dispersion can be filtered to remove any gelled agglomerations.

21
22 The intermediate modified resoles or novolaks that are initially produced in the synthesis are not
23 necessarily water dispersible, but as the chain extension is advanced the resulting chain extended
24 modified resoles or novolaks become progressively more water dispersible by simple mechanical
25 agitation. The chain extension for the dispersed resole is determined by measuring the viscosity of
26 the reaction mixture. Once the resole reaction mixture has reached the desired viscosity, which
27 varies depending upon the reactant composition, the reaction is stopped by removing the heat. The
28 chain extension for the dispersed novolak is determined by pre-selecting the F/P ratio of the total

1 reaction mixture (in other words, the amount of aldehyde compound(s) relative to the amount of
2 phenolic(s) in both the first and second stages). The reaction for the, novolak is allowed to proceed
3 until substantially all the total amount of the reactants have reacted. In other words, there is
4 essentially no unreacted reactant remaining. Preferably, the molecular weight (i.e., chain extension)
5 of the novolak should be advanced to just below the gel point.

6
7 The amount of the novolak dispersion present in the treatment formulations of the invention is not
8 critical. Preferably, it is present in an amount of 1 to 20, more preferably, 2 to 6, weight percent
9 based on the total weight of the non-volatile components of the composition.

10
11 The phenolic resin dispersion forms environmentally (especially corrosion) resistant, non-resolvatable
12 films when applied to a metal surface and cured. As used herein, "non-resolvatable" means that the
13 film does not resolve when an aqueous covercoat is applied to the film before it is thermoset. If the
14 film resolvated, the components of the film would dissolve or disperse into the aqueous covercoat
15 thus destroying any advantage intended from the formation of the film on a surface. The low ionic
16 content of the modified phenolic resin dispersion (relative to water soluble phenolic resins) allows
17 them to behave similarly to non-ionically modified resins and form very water resistant films on
18 curing.

19
20 In one aspect of the technique for coating ferrous metal piping systems, an acid is also incorporated
21 into the aqueous phenolic resin dispersion. The acid can be any acid that is capable of reacting with
22 a metal to generate multivalent ions. Illustrative acids include hydrofluoric acid, phosphoric acid,
23 sulfuric acid, hydrochloric acid and nitric acid. In the case of steel the multivalent ions will be ferric
24 and/or ferrous ions. Aqueous solutions of phosphoric acid are preferred. When the acid is mixed into
25 the composition presumably the respective ions are formed and exist as independent species in
26 addition to the presence of the free acid. In other words, in the case of phosphoric acid, phosphate
27 ions and free phosphoric acid co-exist in the formulated final multi-component composition. The acid
28 preferably is present in an amount of 5 to 300 parts by weight, more preferably 10 to 1609 parts by

weight, based on 100 parts by weight of the phenolic novolak resin dispersion.

Water, preferably deionized water, is utilized in the metal treatment composition of the invention in order to vary the solids content. Although the solids content may be varied as desired, the solids content of the metal treatment composition typically is 1 to 10, preferably 3 to 6%. Since the metal treatment composition is waterborne it is substantially free of volatile organic compounds.

The resulting coating from application of the metal treatment composition is a thin, tightly bound interpenetrating organic/inorganic matrix of phenolic/metal phosphates at the metal substrate interface. This matrix can be further flexibilized with polymers. The flexibilizer is any material that contributes flexibility and/or toughness to the film formed from the composition. The toughness provided by the flexibilizer provides fracture resistance to the film. The flexibilizer should be non-glassy at ambient temperature and be an aqueous emulsion latex or aqueous dispersion that is compatible with the phenolic novolak resin dispersion. The flexibilizer preferably is formulated into the composition in the form of an aqueous emulsion latex or aqueous dispersion.

Suitable flexibilizers include aqueous latices, emulsions or dispersions of (poly)butadiene, neoprene, styrene-butadiene rubber, acrylonitrile-butadiene rubber (also known as nitrile rubber), halogenated polyolefin, acrylic polymer, urethane polymer, ethylene-propylene copolymer rubber, ethylene-propylene-diene terpolymer rubber, styrene-acrylic copolymer, polyamide, poly(vinyl acetate) and the like. Halogenated polyolefins, nitrile rubbers and styrene-acrylic copolymers are preferred.

A suitable styrene-acrylic polymer latex is commercially available from Goodyear Tire & Rubber under the trade designation PLIOTEC and described, for example, in U.S. Pat. Nos. 4,968,741; 5,122,566 and 5,616,635. According to U.S. Pat. No. 5,616,635, such a copolymer latex is made from 45-85 weight percent vinyl aromatic monomers, 15-50 weight percent of at least one alkyl acrylate monomer and 1-6 weight percent unsaturated carbonyl compound. Styrene is the preferred vinyl aromatic monomer, butyl acrylate is the preferred acrylate monomer and acrylic acid and

methacrylic acid are the preferred unsaturated carbonyl compound. The mixture for making the latex also includes at least one phosphate ester surfactant, at least one water-insoluble nonionic surface active agent and at least one free radical initiator.

If nitrile rubber is the flexibilizer, it is preferably mixed into the composition as an emulsion latex. It is known in the art that nitrile rubber emulsion latices are generally made from at least one monomer of acrylonitrile or an alkyl derivative thereof and at least one monomer of a conjugated diene, preferably butadiene. According to U.S. Pat. No. 4,920,176 the acrylonitrile or alkyl derivative monomer should be present in an amount of 0 or 1 to 50 percent by weight based on the total weight of the monomers. The conjugated diene monomer should be present in an amount of 50 percent to 99 percent by weight based on the total weight of the monomers. The nitrile rubbers can also optionally include various co-monomers such as acrylic acid or various esters thereof, dicarboxylic acids or combinations thereof. The polymerization of the monomers typically is initiated via free radical catalysts. Anionic surfactants typically are also added. A suitable nitrile rubber latex is available from B.F. Goodrich under the trade designation HYCAR.

The flexibilizer, if present, preferably is included in the composition in an amount of 5 parts by weight to 300 parts by weight, based on 100 parts by weight phenolic novolak resin dispersion. More preferably, the flexibilizer is present in an amount of 25 parts by weight to 100 parts by weight, based on 100 parts by weight of the phenolic novolak resin dispersion.

The modified phenolic resin dispersion can be cured to form a highly crosslinked thermoset via known curing methods for phenolic resins. The curing mechanism can vary depending upon the use and form of the phenolic resin dispersion. For example, curing of the dispersed resole embodiment typically can be accomplished by subjecting the phenolic resin dispersion to heat. Curing of the dispersed novolak embodiment typically can be accomplished by addition of an aldehyde donor compound.

The aldehyde donor can be essentially be any type of aldehyde known to react with hydroxy aromatic

1 compounds to form cured or crosslinked novolak phenolic resins. Typical compounds useful as an
2 aldehyde (e.g., formaldehyde) source in the present invention include formaldehyde and aqueous
3 solutions of formaldehyde, such as formalin; acetaldehyde; propionaldehyde; isobutyraldehyde; 2-
4 ethylhexaldehyde; 2-methylpentanaldehyde; 2-ethylhexaldehyde; benzaldehyde; as well as compounds
5 which decompose to formaldehyde, such as paraformaldehyde, trioxane, furfural,
6 hexamethylenetetramine, anhydromaldehydianiline, ethylene diamine formaldehyde; acetals which
7 liberate formaldehyde on heating; methylol derivatives of urea and formaldehyde; methylol phenolic
8 compounds; and the like.

9
10 The composition may be applied to a substrate surface by any conventional method such as spraying,
11 dipping, brushing, wiping, roll-coating, or the like, after which the composition is dried. Since in its
12 preferred form, the coating technique allows the compositions to be applied by autodeposition, the
13 compositions are conveniently applied by dipping the metallic substrate or part into a bath of the
14 composition. The metal substrate can reside in the metal treatment composition bath for an amount
15 of time sufficient to deposit a uniform of desired thickness. Typically, the bath residence time is from
16 about 5 to about 120 seconds, preferably about 10 to about 30 seconds, and occurs at room
17 temperature. The metal treatment composition when it is applied to the metal substrate should be
18 sufficiently acidic to cause reaction with the metal to liberate the metallic ions. Typically, the pH of
19 the metal treatment composition should be 1 to 4, preferably 1.5 to 2.5, when it is applied to the metal
20 substrate. The preferred treatment compositions have a solids content of about 7-8% by weight,
21 based upon the total weight of the composition. The composition typically is applied to form a dry
22 film thickness of 1 to 15, preferably 4 to 10 microns.

23
24 After drying, the coated metal surface can be coated with another type of composition. The coated
25 metal substrate typically is dried by subjecting it to heat or forced air. Depending upon the forced
26 air flow, the drying usually occurs at approximately 150-200° F. for a time period ranging from 30
27 seconds to 10 minutes. Alternatively, the treated metal substrate can be stored for a period of time
28 and then subsequently coated with a different composition.

1
2 The coated ferrous metal part may also have an adhesive primer or covercoat applied over the metal
3 treatment. The primer or overcoat does not have to be autodepositable. Conventional, non-
4 autodepositable primers or covercoats can be used with the metal treatment composition. For
5 example, adhesive primers or covercoats such as those described in U.S. Pat. Nos. 3,258,388;
6 3,258,389; 4,119,587; 4,167,500; 4,483,962; 5,036,122; 5,093,203; 5,128,403; 5,200,455;
7 5,200,459; 5,268,404; 5,281,638; 5,300,555; and 5,496,884 may be utilized. Elastomer-to-metal
8 adhesive primers and covercoats are commercially available from Lord Corporation of Huntington,
9 Indiana.

10
11 The treatment formulations of the invention may also utilized without any subsequent coating.

12
13 Preparation of the dispersed aqueous phenolic dispersions of the type useful in the practice of the
14 present invention will now be described in more detail by way of the following non-limiting examples:

15
16 EXAMPLE 1- Preparation of Dispersed Novolak Resin:

17
18 40 g of 6,7-dihydroxy-2-naphthalenesulfonate, sodium salt (available from Andrew Chemicals), 136
19 g. of a water soluble resole (made from formaldehyde and phenol, F/P ratio of 2.3, 80% solids and
20 commercially available from Schenectady under the trade designation HRJ11722), 50 g of tert-butyl
21 catechol and 50 g of water were mixed together and steam heated for approximately three and one-
22 half hours until the mixture became very viscous. 220 g of resorcinol and 220 g of water were added
23 followed by 6 g of phosphoric acid in 20 g of water. Steam heating was continued for another 40
24 minutes. 70 g of formalin then was added while continuing steam heating resulting in a concentrate.
25 The concentrate was filtered and self-dispersed upon the addition of 1730 g of water.

26
27 EXAMPLE 2- Preparation of Dispersed Resole Resin:

1 160 g of 6,7-dihydroxy-2-naphthalenesulfonate, sodium salt (available from Andrew Chemicals), 1000
2 g of the HRJ 11722 water soluble resole, and 50 g of water were mixed together and steam heated
3 for approximately three hours resulting in a very thick concentrate. 3600 g of water was added to the
4 concentrate which then self-dispersed and was filtered.

5
6
7 EXAMPLE 3- Autodepositable Metal Treatment:

8
9 The following ingredients were mixed together in indicated wet weight grams to obtain an
10 autodepositable coating/primer:

| | |
|---|--------|
| 11 Carbon black | 21 g |
| 12 ZnO | 180 g |
| 13 aqueous resole dispersion of Example 1 | 400 g |
| 14 Polyvinyl alcohol-stabilized resole (BKUA 2370) | 600 g |
| 15 Dichlorobutadiene homopolymer (VERSA TL/DOWFAX stabilized) | 450 g |
| 16 Water | 1000 g |

17
18
19 The following ingredients were mixed together in indicated wet weight grams to obtain a metal
20 treatment used as an activator composition:

| | |
|--|--------|
| 21 Aqueous novolak dispersion of Example 2 | 600 g |
| 22 Phosphoric acid | 400 g |
| 23 Water | 2700 g |

Description of the Protective Coating Process for Ferrous Metal Piping Systems:

Figure 1 shows a typical portion of a ductile iron piping system of the type used for fluid conveyance (water, sewage) which would be treated with the coating system of the invention. The piping system 10 includes the ductile iron pipe 8 which is shown at a joint including an external restraining flange or gland 13. The gland 13 is held in place by nuts and bolts 11, 12. The ferrous metal pipe 8 has an interior surface 15 and an exposed exterior surface 17, as well as opposing ends (not shown). Figure 2 shows a partial cross section of the pipe joint, including a male pipe end 19 which is received within a mating female socket end 21. The external gland 13 and retaining nuts and bolts 11, 12 are also illustrated, as well as the annular sealing ring 23. Any of the exposed ferrous metal surfaces of the pipes, components or accessories of the piping system can be coated using the techniques of the invention.

Figure 3 is a flow chart which illustrates the steps in one typical coating operation of the invention in which a ductile iron gland, such as gland 13 in Figure 1 is coated to provide improved corrosion protection. In the first step 25, the metal gland 13 (Figure 1) is dipped in an alkaline cleanser in a first dip tank for contaminant removal. The part is exposed to the cleanser in the tank at a temperature of 160°F for 160 seconds, followed by a 15 second drip time.

In the second step 27, an additional alkaline cleansing step is utilized with the part being dipped at 168°F for 160 seconds, followed by a 5 second drip time.

In the next step 29, another alkaline cleansing step is employed, this time at ambient temperature for 160 seconds followed by a 5 second drip time.

1 In the next step 31, an acid rinse is utilized to bring the iron in the treated part to the surface of the
2 metal.

3
4 The next step 33 is the final metal cleansing utilizing city water as a rinse for 20 seconds, followed
5 by a 8-9 second drip time.

6
7 In the next step 35, a primer coat of the aqueous phenolic resin described above is applied to the part
8 by dipping the part in a bath at 63.1°F for 20 seconds with a drip time of 9 seconds.

9
10 In the next step 37, the part is conveyed to an oven for setting at 240-250°F for 12-13 minutes.

11
12 The next step 39, represents a hanging time of 4 minutes to allow cooling of the part.

13
14 In the next step 41, the corrosion protection coating consisting of the aqueous phenolic dispersion
15 and acid formulation described above is applied to the part by dipping the part in a bath at 65-72°F
16 for 10-12 seconds.

17
18 In the next step 43, the part is baked in a second oven at 240-250°F for 13 minutes.

19
20 In the next step 45, the part is conveyed to a cooling station and hangs for 6 minutes.

21
22 In the next step 47, the product is hung on a conveyor belt and fed to a final 130 foot bake oven
23 where it is baked at 400°F for 20-25 minutes.

1 In the final step 49, the baked and dried parts are inspected for defects.

2
3 Advantages of the Invention:

4
5 An invention has been provided with several advantages. The coating system of the invention uses
6 coatings that are autodepositable. When the treatment composition is applied to an electrochemically
7 active metal the acid reacts with the metal to form multivalent ions (for example, ferric and/or ferrous
8 ions in the case of steel) that appear to cause the treatment composition to deposit on the metal
9 surface a self-limiting, substantially uniform, gelatinous, highly acidic wet film. As the film dries, the
10 remaining phosphoric acid converts the surface to the respective metal compound with the respective
11 negative ion of the acid (for example, metal phosphate in the case of phosphoric acid) forming an
12 interpenetrating network with chelating groups of the aqueous dispersed phenolic novolak resin.

13
14 The autodeposition characteristic is important in providing the required corrosion resistance. It
15 allows for the formation of an exceptionally uniform film. Excellent corrosion resistance is possible
16 only if the entire surface of a metal part is protected with a barrier coating. This requirement is
17 usually difficult to achieve on substrate surfaces that have are curved, irregular, or have internal
18 cavities. The autodepositable nature of the coating system of the invention achieves wetting and thus
19 protection of even complex surfaces.

20
21 Another important advantage of the metal treatment composition is that a bath of the composition
22 does not appear to change in composition as cumulative metal surfaces are dipped in the bath over
23 a period of time. It is believed that the very hydrophilic phenolic resin dispersion immobilizes or
24 coagulates on the metal surface as a swollen wet gel rather than as a precipitate. This characteristic
25 minimizes the buildup of sludge with the accompanying problem of waste disposal.

1 The coating techniques of the invention provide extremely effective corrosion protection for ferrous
2 metals of the type used in piping systems for fluid conveyance in the waterworks industry. As
3 compared to prior art treatments, the coatings of the invention adhere under extreme circumstances.
4 Also, the coatings are relatively temperature and humidity tolerant, making control of these variables
5 less critical. The aqueous based phenolic dispersion is VOC-compliant, and is lacking of odor or
6 fumes. Basically all that is necessary is to top up the application tank at the end of the day, a greatly
7 less strenuous procedure than the sludge removal and disposal inherent in the traditional zinc
8 phosphating process. Both solvent based and aqueous adhesives can also be used with the coatings
9 of the invention.

10
11 While the invention has been shown in only one of its forms, it is not thus limited but is susceptible
12 to various changes and modifications without departing from the spirit thereof.